(54) **BIAXIALLY ORIENTED FILM**

(57)   The invention relates to a biaxially oriented film comprising a multimodal high density polyethylene (HDPE1), wherein HDPE1 has a density determined according to ISO 1183 in the range of 952 to 968 kg/m^3 and an MFR_2 determined at 190 °C according to ISO 1133 of 0.3 to 3.0 g/10 min, and wherein HDPE1 comprises at least two fractions:
(A) 30 to 70 wt%, relative to the total weight of HDPE1, of a lower molecular weight fraction being a polyethylene with a density in the range of 955 to 980 kg/m^3 and an MFR_2 of 100 to 2000 g/10 min; and
(B) 30 to 70 wt%, relative to the total weight of HDPE1, of a higher molecular weight fraction being a polyethylene with a density in the range of 925 to 970 kg/m^3 and an MFR_2 of 0.0001 to 1.0 g/10 min;
and wherein said film further comprises 1 to 30 wt%, relative to the total weight of the film, of a second HDPE (HDPE2) with a density in the range of 955 to 985 kg/m^3 and an MFR_2 of 5 to 100 g/10 min, and which is different to HDPE1.

(52) Cooperative Patent Classification (CPC): (Cont.)

C-Sets
C08F 210/16, C08F 4/6492;
C08L 23/06, C08L 23/06;
C08F 110/02, C08F 2500/12, C08F 2500/07;
C08F 210/16, C08F 210/08, C08F 2500/12,
C08F 2500/07, C08F 2500/30, C08F 2500/26

Description

[0001]   This invention relates to a biaxially oriented film with beneficial mechanical, processing and optical properties. In particular, the invention relates to a biaxially oriented film, comprising two different high density polyethylenes (HDPEs), with improved properties. The invention further relates to laminates comprising the film.

Background of Invention

[0002]   Polymer films are widely used in packaging. These films must obviously protect the contents of the package from damage and the environment.

[0003]   Polyethylene films are widely used in packaging and are often laminated with a relatively high heat resistant substrate like PET film to prepare a flexible package. However, such laminates cannot be readily recycled due to the presence of two chemically different materials.

[0004]   To resolve that problem a machine direction oriented polyethylene (MDO PE) or biaxially oriented polyethylene (BOPE) film can be used to replace the PET film. HDPE offers a good alternative to PET in terms of stiffness and thermal resistance. The resulting laminate comprises polyethylene only and therefore can be fully mechanically recycled.

[0005]   Biaxial orientation of polyolefin films is a well-known and well established technology. The polymer requires stiffness at elevated temperature otherwise the film will break. A downside of the ability to withstand the elevated temperature stretching procedure is however, that biaxially oriented films made from HDPE result in very stiff and at the same time brittle, opaque, hazy and/or matt films.

[0006]   There is thus a need to produce films which show better stiffness, together with good impact and optical properties. It is further desired that the films show these improved mechanical properties regardless of the orientation of the films. That means films should provide good mechanical properties in both the machine (MD) and transverse direction (TD). Isotropic behaviour of stiffness and low shrinkage is also attractive.

[0007]   The need to provide such biaxially oriented films with well-balanced mechanical and optical properties as well as low and isotropic shrinkage behaviour is also triggered by the desire to provide monomaterial packaging solutions which meet the increasing demand on easy recyclability.

[0008]   WO 98/14491 describes a biaxially oriented film of high density polyethylene. The HDPE may have a density of 940 kg/m^3 or higher and a melt index in the range of 0.5 to 10 g/10 min. HDPE blends are envisaged, which are stated to advantageously include a major proportion of an HDPE having a melt index of 0.5 to 2 g/10 min. US 5885721 contains a similar disclosure.

[0009]   WO 2020/257411 discloses a multilayer film comprising a core layer which contains at least 50 wt% of an HDPE and outer layers comprising ethylenepropylene polymers.

[0010]   The present inventors have unexpectedly found that a biaxially oriented film comprising a particular class of multimodal HDPE (referred to herein as HDPE1) and a second HDPE which is different to the multimodal HDPE (referred to herein as HDPE2) possesses an attractive balance of stiffness and haze. In particular, it has been found that the combination of these two different HDPEs provides an improved material for biaxially oriented film applications, which combines very good mechanical properties e.g. in terms of tensile modulus, with excellent optical properties e.g. in terms of haze.

Summary of Invention

[0011]   Viewed from one aspect the invention provides a biaxially oriented film comprising a multimodal high density polyethylene (HDPE1), wherein HDPE1 has a density determined according to ISO 1183 in the range of 952 to 968 kg/m^3 and an MFR$_2$ determined at 190 °C according to ISO 1133 of 0.3 to 3.0 g/10 min, and wherein HDPE1 comprises at least two fractions:

   (A) 30 to 70 wt%, relative to the total weight of HDPE1, of a lower molecular weight fraction being a polyethylene with a density in the range of 955 to 980 kg/m^3 and an MFR$_2$ of 100 to 2000 g/10 min; and
   (B) 30 to 70 wt%, relative to the total weight of HDPE1, of a higher molecular weight fraction being a polyethylene with a density in the range of 925 to 970 kg/m^3 and an MFR$_2$ of 0.0001 to 1.0 g/10 min;

and wherein said film further comprises 1 to 30 wt%, relative to the total weight of the film, of a second HDPE (HDPE2) with a density in the range of 955 to 985 kg/m^3 and an MFR$_2$ of 5 to 100 g/10 min, and which is different to HDPE1.

[0012]   Viewed from a second aspect, the invention provides a laminated film structure comprising a biaxially oriented film as hereinbefore defined laminated to a substrate.

Detailed Description

Multimodal High Density Polyethylene (HDPE1)

[0013] The multimodal high density ethylene polymer (HDPE1) may be a homopolymer or a copolymer, but is preferably an ethylene copolymer. By ethylene copolymer is meant a polymer the majority by weight of which derives from ethylene monomer units (i.e. at least 50 wt% ethylene relative to the total weight of the copolymer). The comonomer contribution preferably is up to 10 % by mol, more preferably up to 5 % by mol.

[0014] The other copolymerisable monomer or monomers are preferably C3-12, especially C3-10, alpha olefin comonomers, particularly singly or multiply ethylenically unsaturated comonomers, in particular C3-10-alpha olefins such as propene, 1-butene, 1-hexene, 1-octene, and 4-methyl-1-pentene. The use of 1-hexene, 1-octene and 1-butene, or mixtures thereof, is particularly preferred, especially 1-hexene and 1-butene. Ideally there is only one comonomer present.

[0015] HDPE1 is multimodal and therefore comprises at least two components. HDPE1 is preferably bimodal. HDPE1 most preferably comprises

(A) a lower molecular weight ethylene homopolymer component, and
(B) a higher molecular weight ethylene copolymer component.

[0016] Usually, a polyethylene composition comprising at least two polyethylene fractions, which have been produced under different polymerisation conditions resulting in different (weight average) molecular weights and molecular weight distributions for the fractions, is referred to as "multimodal". Accordingly, in this sense the compositions of the invention are multimodal polyethylenes. The prefix "multi" relates to the number of different polymer fractions the composition is consisting of. The polyethylene may also be multimodal with respect to comonomer content.

[0017] The form of the molecular weight distribution curve, i.e. the appearance of the graph of the polymer weight fraction as a function of its molecular weight, of such a multimodal polyethylene will show two or more maxima or at least be distinctly broadened in comparison with the curves for the individual fractions.

[0018] For example, if a polymer is produced in a sequential multistage process, utilising reactors coupled in series and using different conditions in each reactor, the polymer fractions produced in the different reactors will each have their own molecular weight distribution and weight average molecular weight. When the molecular weight distribution curve of such a polymer is recorded, the individual curves from these fractions are superimposed into the molecular weight distribution curve for the total resulting polymer product, usually yielding a curve with two or more distinct maxima.

[0019] HDPE1 of the invention has an MFR_2 determined at 190 °C according to ISO 1133 of 0.3 to 3.0 g/10 min. Preferable ranges for MFR_2 are 0.4 to 2.5 g/10min, such as 0.5 to 2.0 g/10min, or such as 0.6 to 1.0 g/10 min.

[0020] HDPE1 of the invention preferably has an MFR_{21} determined at 190 °C according to ISO 1133 of 15 to 80 g/10min, such as 20 to 75 g/10 min, most preferably 30 to 65 g/10 min.

[0021] HDPE1 of the invention preferably has a Flow Rate Ratio (FRR) of the MFR_{21}/MFR_2 of at least 25.0, like at least 35.0, more preferably at least 45.0. Furthermore, HDPE1 of the invention preferably has a Flow Rate Ratio (FRR) of the MFR_{21}/MFR_2 of up to 80.0, like up to 75.0, more preferably up to 70.0.

[0022] The density of HDPE1 is in the range 952 to 968 kg/m^3 determined according to ISO 1183. HDPE1 is therefore a high density polyethylene. Preferably, HDPE1 has a density of 953 to 965 kg/m^3, more preferably 954 to 963 kg/m^3, such as 955 to 961 kg/m^3.

[0023] HDPE1 of the invention preferably has a molecular weight distribution (MWD) in the range 7 to 30, such as 10 to 20, and most preferably 11 to 15.

[0024] HDPE1 of the invention comprises at least a lower molecular weight component (A) and a higher molecular weight component (B). In one particularly preferable embodiment, HDPE1 consists of components (A) and (B). The weight ratio of fraction (A) to fraction (B) in the composition is in the range 30:70 to 70:30, more preferably 35:65 to 65:35, most preferably 40:60 to 60:40. In some embodiments the ratio may be 35 to 50 wt% of fraction (A) and 50 to 65 wt% fraction (B), such as 40 to 50 wt% of fraction (A) and 50 to 60 wt% fraction (B), wherein the wt% values are relative to the total weight of HDPE1.

[0025] In a particularly preferred embodiment, the wt% values for fractions (A) and (B) add up to 100 %.

[0026] Each of Fraction (A) and Fraction (B) may be an ethylene homopolymer or an ethylene copolymer. By ethylene homopolymer is meant a polymer comprising at least 97 mol% (such as at least 98 mol%, especially at least 99.5 mol%) ethylene monomer units. The term "ethylene copolymer" is defined above. Most preferably, fraction (A) is an ethylene homopolymer and fraction (B) is an ethylene copolymer.

[0027] HDPE1 of the invention is produced in a multistage process wherein fractions (A) and (B) are produced in subsequent stages. In such a case, the properties of the fractions produced in the second step (or further steps) of the multistage process can either be inferred from polymers which are separately produced in a single stage by applying identical polymerisation conditions (e.g. identical temperature, partial pressures of the reactants/diluents, suspension

medium, reaction time) with regard to the stage of the multistage process in which the fraction is produced, and by using a catalyst on which no previously produced polymer is present. Alternatively, the properties of the fractions produced in a higher stage of the multistage process may also be calculated, e.g. in accordance with B. Hagström, Conference on Polymer Processing (The Polymer Processing Society), Extended Abstracts and Final Programme, Gothenburg, August 19 to 21, 1997, 4:13. Thus, although not directly measurable on the multistage process products, the properties of the fractions produced in higher stages of such a multistage process can be determined by applying either or both of the above methods. The skilled person will be able to select the appropriate method.

[0028]   Polymer HDPEs produced in a multistage process are also designated as *"in-situ"* blends. The resulting end product consists of an intimate mixture of the polymers from the two or more reactors, the different molecular-weight-distribution curves of these polymers together forming a molecular-weight-distribution curve having a broad maximum or two or more maxima, i.e. the end product is a multimodal polymer mixture.

[0029]   The lower molecular weight fraction (A) has an MFR_2 determined at 190 °C according to ISO 1133 of 100 to 2000 g/10min, preferably of 125 to 1500 g/10min, more preferably 150 to 1000 g/10min, such as 200 to 750 g/10 min, or such as 220 to 500 g/10 min.

[0030]   Fraction (A) has a density determined according to ISO 1183 of 955 to 980 kg/m^3, preferably 960 to 978 kg/m^3, such as 965 to 975 kg/m^3.

[0031]   Fraction (A) can be an ethylene homopolymer or copolymer. Preferably, Fraction (A) is an ethylene homopolymer.

[0032]   The higher molecular weight fraction (B) has an MFR_2 determined at 190 °C according to ISO 1133 of 0.0001 to 1.0 g/10min, preferably of 0.0005 to 0.5 g/10min, more preferably 0.0008 to 0.1 g/10min, such as 0.001 to 0.05 g/10 min.

[0033]   Fraction (B) has a density determined according to ISO 1183 of 925 to 970 kg/m^3, preferably 930 to 960 kg/m^3, such as 935 to 950 kg/m^3.

[0034]   Fraction (B) can be an ethylene homopolymer or copolymer. Fraction (B) is preferably a copolymer. Preferred ethylene copolymers employ alpha-olefins (e.g. C3-12 alpha-olefins) as comonomers. Examples of suitable alpha-olefins include 1-butene, 1-hexene and 1-octene. 1-butene is an especially preferred comonomer.

Preparation of HDPE1

[0035]   HDPE1 may be produced by polymerisation using conditions which create a multimodal (e.g. bimodal) polymer product ideally using a Ziegler Natta catalyst system. Typically, a two or more stage, i.e. multistage, polymerisation process is used with different process conditions in the different stages or zones (e.g. different temperatures, pressures, polymerisation media, hydrogen partial pressures, etc). Preferably, the multimodal (e.g. bimodal) composition is produced by a multistage polymerisation, e.g. using a series of reactors, with optional comonomer addition preferably in only the reactor(s) used for production of the higher/highest molecular weight component(s). A multistage process is defined to be a polymerisation process in which a polymer comprising two or more fractions is produced by producing each or at least two polymer fraction(s) in a separate reaction stage, usually with different reaction conditions in each stage, in the presence of the reaction product of the previous stage which comprises a polymerisation catalyst. The polymerisation reactions used in each stage may involve conventional ethylene homopolymerisation or copolymerisation reactions, e.g. gas-phase, slurry phase, liquid phase polymerisations, using conventional reactors, e.g. loop reactors, gas phase reactors, batch reactors etc. (see for example WO97/44371 and WO96/18662).

[0036]   Preferably, HDPE1 is a bimodal HDPE prepared in a two-stage polymerisation process.

[0037]   The first polymerisation stage produces an ethylene homopolymer or an ethylene copolymer, typically an ethylene homopolymer, which is subsequently fed to the second polymerisation stage. The second polymerisation stage can produce a further ethylene homopolymer, or an ethylene copolymer, preferably an ethylene copolymer.

[0038]   The first polymerisation stage is preferably a slurry polymerisation step.

[0039]   The slurry polymerisation usually takes place in an inert diluent, typically a hydrocarbon diluent such as methane, ethane, propane, n-butane, isobutane, pentanes, hexanes, heptanes, octanes etc., or their mixtures. Preferably the diluent is a low-boiling hydrocarbon having from 1 to 4 carbon atoms or a mixture of such hydrocarbons. An especially preferred diluent is propane, possibly containing minor amounts of methane, ethane and/or butane.

[0040]   The ethylene content in the fluid phase of the slurry may be from 1 to 50 % by mole, preferably from 2 to 20 % by mole and in particular from 2 to 10 % by mole. The benefit of having a high ethylene concentration is that the productivity of the catalyst is increased but the drawback is that more ethylene then needs to be recycled than if the concentration was lower.

[0041]   The temperature in the first polymerisation stage is typically from 60 to 110 °C, preferably from 70 to 100 °C. An excessively high temperature should be avoided to prevent partial dissolution of the polymer into the diluent and the fouling of the reactor. The pressure is generally from 1 to 150 bar, preferably from 40 to 80 bar.

[0042]   The slurry polymerisation may be conducted in any known reactor used for slurry polymerisation. Such reactors include a continuous stirred tank reactor and a loop reactor. It is especially preferred to conduct the slurry polymerisation

in a loop reactor. In such reactors the slurry is circulated with a high velocity along a closed pipe by using a circulation pump. Loop reactors are generally known in the art and examples are given, for instance, in US-A-4582816, US-A-3405109, US-A-3324093, EP-A-479186 and US-A-5391654. It is thus preferred to conduct the first polymerisation stage as a slurry polymerisation in a loop reactor.

[0043] The slurry may be withdrawn from the reactor either continuously or intermittently. A preferred way of intermittent withdrawal is the use of settling legs where slurry is allowed to concentrate before withdrawing a batch of the concentrated slurry from the reactor. The use of settling legs is disclosed, among others, in US-A-3374211, US-A-3242150 and EP-A-1310295. Continuous withdrawal is disclosed, among others, in EP-A-891990, EP-A-1415999, EP-A-1591460 and WO-A-2007/025640. The continuous withdrawal is advantageously combined with a suitable concentration method, as disclosed in EP-A-1310295 and EP-A-1591460. It is preferred to withdraw the slurry from the first polymerisation stage continuously.

[0044] Hydrogen is typically introduced into the first polymerisation stage for controlling the MFR_2 of the resultant polymer. The amount of hydrogen needed to reach the desired MFR depends on the catalyst used and the polymerisation conditions. The desired polymer properties may be obtained in slurry polymerisation in a loop reactor with the molar ratio of hydrogen to ethylene of from 100 to 1000 mol/kmol (or mol/1000 mol) and preferably of from 200 to 800 mol/kmol.

[0045] The average residence time in the first polymerisation stage is typically from 20 to 120 minutes, preferably from 30 to 80 minutes. As it is well known in the art the average residence time τ can be calculated from Equation 1 below:

$$\text{Equation 1: Residence Time}$$

$$\tau = \frac{V_R}{Q_o}$$

[0046] Where V_R is the volume of the reaction space (in case of a loop reactor, the volume of the reactor, in case of the fluidized bed reactor, the volume of the fluidized bed) and Q_o is the volumetric flow rate of the product stream (including the polymer product and the fluid reaction mixture).

[0047] The production rate is suitably controlled with the catalyst feed rate. It is also possible to influence the production rate by suitable selection of the monomer concentration. The desired monomer concentration can then be achieved by suitably adjusting the ethylene feed rate.

[0048] In the second polymerisation stage, ethylene is polymerised, optionally together with at least one alpha-olefin comonomer, in the presence of the catalyst and the ethylene polymer produced in the first polymerisation stage. It will thus be appreciated that the second polymerisation stage generates an ethylene polymer, which combines with the ethylene polymer from the first polymerisation stage, to form the multimodal HDPE1. Preferable comonomers are discussed hereinbefore, however it is noted that it is particularly preferable if the at least one alpha-olefin is 1-butene.

[0049] The second polymerisation stage is preferably a gas phase polymerisation step, i.e. carried out in a gas-phase reactor. Any suitable gas phase reactor known in the art may be used, such as a fluidised bed gas phase reactor.

[0050] For gas phase reactors, the reaction temperature used will generally be in the range 60 to 115°C (e.g. 70 to 110°C), the reactor pressure will generally be in the range 10 to 25 bar, and the residence time will generally be 1 to 8 hours. The gas used will commonly be a non-reactive gas such as nitrogen or low boiling point hydrocarbons such as propane together with monomer (e.g. ethylene).

[0051] A chain transfer agent (e.g. hydrogen) is typically added to the second polymerisation stage, preferably in amounts of 50 to 500 mol of H_2/kmol ethylene.

[0052] The split between the first polymerisation stage and the second polymerisation stage (i.e. between the slurry polymerisation and the gas phase polymerisation) is typically 30:70 to 70:30, more preferably 35:65 to 65:35, most preferably 40:60 to 60:40.

Prepolymerisation

[0053] The polymerisation steps discussed above may be preceded by a prepolymerisation step. The purpose of the prepolymerisation is to polymerise a small amount of polymer onto the catalyst at a low temperature and/or a low monomer concentration. By prepolymerisation it is possible to improve the performance of the catalyst in slurry and/or modify the properties of the final polymer. The prepolymerisation step is conducted in slurry.

[0054] Thus, the prepolymerisation step may be conducted in a loop reactor. The prepolymerisation is then preferably conducted in an inert diluent, typically a hydrocarbon diluent such as methane, ethane, propane, n-butane, isobutane, pentanes, hexanes, heptanes, octanes etc., or their mixtures. Preferably the diluent is a low-boiling hydrocarbon having from 1 to 4 carbon atoms or a mixture of such hydrocarbons.

[0055] The temperature in the prepolymerisation step is typically from 0 to 90 °C, preferably from 20 to 80 °C and

more preferably from 55 to 75 °C.

[0056] The pressure is not critical and is typically from 1 to 150 bar, preferably from 40 to 80 bar.

[0057] The amount of monomer is typically such that from 0.1 to 1000 grams of monomer per one gram of solid catalyst component is polymerised in the prepolymerisation step. As the person skilled in the art knows, the catalyst particles recovered from a continuous prepolymerisation reactor do not all contain the same amount of prepolymer. Instead, each particle has its own characteristic amount which depends on the residence time of that particle in the prepolymerisation reactor. As some particles remain in the reactor for a relatively long time and some for a relatively short time, then also the amount of prepolymer on different particles is different and some individual particles may contain an amount of prepolymer which is outside the above limits. However, the average amount of prepolymer on the catalyst typically is within the limits specified above.

[0058] The molecular weight of the prepolymer may be controlled by hydrogen as it is known in the art. Further, antistatic additives may be used to prevent the particles from adhering to each other or the walls of the reactor, as disclosed in WO-A-96/19503 and WO-A-96/32420.

[0059] The catalyst components are preferably all introduced to the prepolymerisation step when a prepolymerisation step is present. However, where the solid catalyst component and the cocatalyst can be fed separately it is possible that only a part of the cocatalyst is introduced into the prepolymerisation stage and the remaining part into subsequent polymerisation stages. Also in such cases it is necessary to introduce so much cocatalyst into the prepolymerisation stage that a sufficient polymerisation reaction is obtained therein.

[0060] It is understood within the scope of the invention, that the amount of polymer produced in the prepolymerisation typically lies within 1 - 5 wt% in respect to the final HDPE1.

Catalyst

[0061] The polymerisation is typically conducted in the presence of a Ziegler-Natta polymerisation catalyst. Suitable Ziegler-Natta (ZN) catalysts generally comprise at least a catalyst component formed from a transition metal compound of Group 4 to 6 of the Periodic Table (IUPAC, Nomenclature of Inorganic Chemistry, 1989), a metal compound of Group 1 to 3 of the Periodic Table (IUPAC), optionally a compound of group 13 of the Periodic Table (IUPAC), and optionally an internal organic compound, like an internal electron donor. A ZN catalyst may also comprise further catalyst component(s), such as a cocatalyst and optionally external additives.

[0062] Suitable ZN catalysts preferably contain a magnesium compound, an aluminium compound and a titanium compound supported on a particulate support.

[0063] The particulate support can be an inorganic oxide support, such as silica, alumina, titania, silica-alumina, silica-titania or a $MgCl_2$ based support. Preferably, the support is silica or a $MgCl_2$ based support.

[0064] Particularly preferred Ziegler-Natta catalysts are such as described in EP 1378528 A1 and in EP 2994506 B1.

[0065] If used, the magnesium compound preferably is a reaction product of a magnesium dialkyl and an alcohol. The alcohol is a linear or branched aliphatic monoalcohol. Preferably, the alcohol has from 6 to 16 carbon atoms. Branched alcohols are especially preferred, and 2-ethyl-1-hexanol is one example of the preferred alcohols. The magnesium dialkyl may be any compound of magnesium bonding to two alkyl groups, which may be the same or different. Butyl-octyl magnesium is one example of the preferred magnesium dialkyls.

[0066] The aluminium compound is a chlorine containing aluminium alkyl. Especially preferred compounds are aluminium alkyl dichlorides and aluminium alkyl sesquichlorides.

[0067] The transition metal compound of Group 4 to 6 is preferably a titanium or vanadium compound, more preferably a halogen containing titanium compound, most preferably chlorine containing titanium compound. An especially preferred titanium compound is titanium tetrachloride.

[0068] The catalyst can be prepared by sequentially contacting the carrier with the above mentioned compounds, as described in EP 688794 or WO 99/51646. Alternatively, it can be prepared by first preparing a solution from the components and then contacting the solution with a carrier, as described in WO 01/55230.

[0069] Another group of suitable ZN catalysts contain a titanium compound together with a magnesium halide compound acting as a support. Thus, the catalyst contains a titanium compound and optionally a Group 13 compound for example an aluminium compound on a magnesium dihalide, like magnesium dichloride. Such catalysts are disclosed, for instance, in WO 2005/118655, EP 810235, WO 2014/096296 and WO 2016/097193.

[0070] Suitable activators are group 13 metal compounds, typically group 13 alkyl compounds and especially aluminium alkyl compounds, where the alkyl group contains 1 to 16 C-atoms. These compounds include trialkyl aluminium compounds, such as trimethylaluminium, triethylaluminium, tri-isobutylaluminium, trihexylaluminium and tri-n-octylaluminium, alkyl aluminium halides, such as ethylaluminium dichloride, diethylaluminium chloride, ethylaluminium sesquichloride, dimethylaluminium chloride and the like. Especially preferred activators are trialkylaluminiums, of which triethylaluminium, trimethylaluminium and tri-isobutylaluminium are particularly used.

[0071] The amount in which the activator is used depends on the specific catalyst and activator. Typically, triethyla-

luminium is used in such amount that the molar ratio of aluminium to the transition metal, like Al/Ti, is from 1 to 1000, preferably from 3 to 100 and in particular from about 5 to about 30 mol/mol.

[0072] An optional internal organic compound may be chosen from the following classes: ethers, esters, amines, ketones, alcohols, anhydrides or nitriles or mixtures thereof. Preferably, the optional internal organic compound is selected from ethers and esters, most preferably from ethers. Preferred ethers are of 2 to 20 carbon-atoms and especially mono, di or multi cyclic saturated or unsaturated ethers comprising 3 to 6 ring atoms. Typical cyclic ethers suitable in the present invention, if used, are tetrahydrofuran (THF), substituted THF, like 2-methyl THF, di-cyclic ethers, like 2,2-di(2-tetrahydrofuryl)propane, 2,2-di-(2-furan)-propane, or isomers or mixtures thereof. Internal organic compounds are also often called as internal electron donors.

[0073] In the production of HDPE1, preferably a compounding step is applied, wherein the composition of the base resin, i.e. the blend, which is typically obtained as a base resin powder from the reactor, is extruded in an extruder and then pelletised to polymer pellets in a manner known in the art.

[0074] HDPE1 may also contain minor quantities of additives such as pigments, nucleating agents, antistatic agents, fillers, antioxidants, etc., generally in amounts of up to 10 % by weight, preferably up to 5 % by weight.

[0075] Optionally, additives or other polymer components can be added to HDPE1 during the compounding step in the amount as described above. Preferably, HDPE1 obtained from the reactor is compounded in the extruder together with additives in a manner known in the art.

[0076] The film typically comprises 70 to 99 wt%, preferably 75 to 95 wt%, relative to the total weight of the film, of HDPE1.

HDPE2

[0077] The film further comprises 1 to 30 wt%, preferably 5 to 25 wt%, relative to the total weight of the film, of an HDPE (referred to herein as HDPE2), which is different to the multimodal HDPE1 of the invention.

[0078] HDPE2 has a density of 955 to 985 kg/m^3 determined according to ISO1183, preferably 957 to 980 kg/m^3, such as 960 to 970 kg/m^3.

[0079] HDPE2 has an MFR$_2$ determined at 190 °C according to ISO 1133 of 5 to 100 g/10 min, preferably 8 to 60 g/10 min, such as 10 to 50 g/10 min, or such as 20 to 40 g/10 min.

[0080] HDPE2 may be a homopolymer or a copolymer, but is preferably an ethylene copolymer. The other copolymerisable monomer or monomers are preferably C3-12, especially C3-10, alpha olefin comonomers, particularly singly or multiply ethylenically unsaturated comonomers, in particular C3-10-alpha olefins such as propene, 1-butene, 1-hexene, 1-octene, and 4-methyl-1-pentene. The use of 1-hexene, 1-octene and 1-butene, or mixtures thereof, is particularly preferred, especially 1-hexene and 1-butene. Ideally there is only one comonomer present, which is preferably 1-butene.

[0081] HDPE2 of the invention may be unimodal or multimodal. When HDPE2 is multimodal, it is preferred that it is bimodal with two different fractions having different molecular weight.

[0082] HDPE2 may contain minor quantities of additives such as pigments, nucleating agents, antistatic agents, fillers, antioxidants, etc., generally in amounts of up to 10 % by weight, preferably up to 5 % by weight relative to the total weight of HDPE2.

Film

[0083] The film of the invention is a biaxially oriented film. The biaxially oriented films of the present invention can have a thickness in the range of 5.0 - 100 μm, such as 10.0 - 75.0 μm, like 15.0 - 50 μm or 20.0 - 40.0 μm.

[0084] The biaxially oriented films of the present invention show good optical properties in view of haze transparency when measured according to ASTM D1003. A possible range for the haze is 0.5 to 20.0%. The haze is typically 14.0 % or lower, such as 9.0 % or lower, such as 8.0 or 5.0% or lower. The haze may be in the range of 0.5 to 9.0, preferably 1.0 to 8.0, more preferably 1.5 to 5.0, such 1.5 to 4.0. Preferably the measurements for haze are done 20 μm films.

[0085] Further, it is preferred that the film has a tensile modulus (TM) determined according to ISO 527-3 on 20μm films in machine direction (MD) of at least 1000 MPa to 4000 MPa, more preferably in the range of 1500 to 3000 MPa, still more preferably in the range of 1700 to 2500 MPa.

[0086] The films of the invention ideally have a stretch ratio in the machine direction (MD) and/or transverse direction (TD) of more than 5.0 times, preferably at least 6.0 times, more preferably at least 7.0 times, such as at least 8.0 times.

[0087] In one embodiment of the invention, the films consist essentially of HDPE1 and HDPE2. The term consists essentially of means that the polymers as hereinbefore defined are the only "non additive" polyolefins present. It will be appreciated however that such polymers may contain standard polymer additives some of which might be supported on a polyolefin (a so called masterbatch as is well known in the art). The term consists essentially of does not exclude the presence of such a supported additive.

[0088] In an alternative embodiment, HDPE1 and HDPE2 can be blended with other polymers in the biaxially oriented

films of the invention.

[0089] If other polymers are present, it is preferred if any other polymer is a polyethylene. Thus, in a preferred embodiment, the biaxially oriented articles of the present invention are characterised by being free of any polymers other than polyethylenes. Suitable polyethylenes that can be mixed include HDPE, MDPE, LLDPE, LDPE and ethylene based plastomers and elastomers.

[0090] The biaxially oriented films of the present invention may contain usual polymer additives, such as slip agents, UV-stabilisers, pigments, antioxidants, nucleating agents and so on. These additives may be carried on a carrier polymer in the form of a masterbatch.

[0091] For the avoidance of doubt, it is envisaged that usual polymer additives, e.g. as described above may be present even when the film, (or even a film layer) "consists" of HDPE1 and HDPE2. The term "consists of" is not intended therefore to exclude the presence of polymer additives. It does however exclude the presence of other polymer components for blending with the HDPE1 and HDPE2. If a carrier polymer is used as part of a masterbatch, that is not excluded however. Articles may be free of any other mixing polymers but may still comprise minor amounts of carrier polymer used for masterbatches.

[0092] The biaxially oriented films of the present invention can be monolayer films or multilayer films. Multilayer films may comprise 2 or more layers, such as 3, 5, 7 or more layers. Preferably, the film is a monolayer film.

[0093] If the biaxially oriented film is a multilayer film, HDPE1 and HDPE2 may be present in a core layer or in any outer layer. In a preferred embodiment, the biaxially oriented film of the present invention is a multilayer film having a core and one or more adjacent layers (e.g. two outer layers), wherein the core layer comprises HDPE1 and HDPE2 and the outer layers comprise low melting polyethylene grades (e.g. LLDPE) which have low density, and are suitable for good sealing behaviour. Suitable outer layers can comprise LLDPE, LDPE or other polyethylene grades, such as elastomers or plastomers preferably having a density of at most 929 kg/m^3, such as 860 to 925 kg/m^3, such as 875 - 920 kg/m^3. The person skilled is well aware what materials can be used as sealing layers.

[0094] HDPE1 and HDPE2 may together form at least 1.0 wt% of the layer in the film in which they are present. It is preferred that a layer within the biaxially oriented film comprises between 1.0 and 100 wt% of HDPE1 and HDPE2 taken together, relative to the total weight of the layer, such as at least 30.0 wt%, or at least 50.0 wt% or at least 70.0 wt%. It is further preferred that a layer of a film comprises HDPE1 and HDPE2 together in amounts in the range of 30.0 - 98.0 wt%, such as 50.0 - 95.0 or 70.0 - 85.0 wt%. The layer may consist of HDPE1 and HDPE2.

[0095] In case the biaxially oriented film of the present invention is a multilayer film, the layer distribution should be as such that the layer comprising HDPE1 and HDPE2 forms a major part of the film structure and the sealing layers form a minor part. Possible layer distributions may be outer layer 1.0 - 25.0 %, core layer 50.0 - 98.0 %, outer layer 1.0 - 25.0 %, wherein the percentages are seen in relation to the total thickness of the film. It is preferred, that each of the outer layers forms 3.0 - 20.0%, such as 4.0 - 15.0 % or 5.0 - 10.0% of the total thickness of the film, and the core layer preferably has 60.0 - 94.0 %, preferably 70 - 92 %, such as 80 - 90 % of the total film thickness.

[0096] The multilayer films of the present invention can be symmetric (with both outer layers having the same thickness, or asymmetric (with just one outer layer or with two or more outer layers differing in view of their thickness.

[0097] The biaxially oriented films of the present invention can be laminated to other substrates to form a laminated structure. Suitable substrates include but are not limited to, biaxially oriented polypropylene film, oriented PET film, oriented polyamide film, blown and cast PE film, aluminum foil and paper. In particular, the substrate to which the biaxial film of the invention is laminated is preferably a polyethylene film. In this way, the entire laminate is formed from polyethylene based polymers.

[0098] It is preferred if the laminate is formed from a mono or multilayer biaxial film as defined herein and a substrate layer, such as a polyethylene substrate layer. That substrate layer is most especially a polyethylene blown film such as one comprising HDPE, MDPE, LLDPE, LDPE and ethylene based plastomers and elastomers.

[0099] In any such laminate, there is preferably one film layer based on the biaxially oriented film of the invention. Such a biaxially oriented film layer within a laminated structure can have a thickness in the range of 5.0 - 100 μm, such as 10.0 - 75.0 μm, like 15.0 - 50 μm or 20.0 - 40.0 μm. The substrate layer may have a thickness of 5.0 - 100 μm, such as 10.0 - 75.0 μm, like 15.0 - 50 μm or 20.0 - 40.0 μm.

[0100] The biaxially oriented films or laminates of the present invention may be used for the production of packaging articles like bags, pouches, labels or lids, or other technical applications like banknotes. The biaxially oriented films or laminates of the present invention are preferably used for applications related to food packaging.

[0101] The manufacture of biaxially oriented films is well known (e.g. chapter 2 and 3 in Biaxial stretching of film: principles and applications, edited by Mark T. DeMeuse, Woodhead Publishing, 2011). The person skilled in the art can apply his knowledge of BOPP film production to the manufacture of the BOPE films of the invention. The films of the invention may be manufactured by any known technology, such as the double bubble, tenter frame or spontaneous process.

[0102] In a typical process, the components of the film are initially mixed and melted within an extruder. The temperature within the extruder is conventional and will be sufficient to ensure melting of the components. The extrudate is cast to

form a cast film (or flat film) which is then cooled. The film should ideally be cooled to a temperature of less than 50 °C before any reheating process is begun. The film is then reheated and stretching is begun. The temperature during the stretching phase can vary and may decrease as the stretching process continues. The reheat temperature in step d) is defined as the temperature at the start of the stretching process. Once stretching in the machine direction is complete, the film is annealed. This maintains the MDO film structure for the TD stretch. Reheating for the second stretching phase is carried out and again, the temperature can vary during the stretching phase. The reheat temperature in step g) is defined therefore as the temperature at the start of the second stretch procedure. Finally, the film is allowed to cool.

Description of Figures

Figure 1: Melt Pressure of Inventive and Comparative examples

[0103]   The present invention will now be described in further detail by the examples provided below:
The following definitions of terms and determination methods apply for the above general description of the invention as well as to the below examples unless otherwise defined.

Determination methods

Melt Flow Rate (MFR)

[0104]   The melt flow rates were measured at 190 °C with a load of 2.16 kg (MFR_2) or 21.6 kg (MFR_{21}) according to ISO 1133

Calculation of MFR_2 of Fractions (A) and (B)

[0105]

$$logA = x \cdot logB + (1 - x) \cdot logC$$

$$C = 10^{\wedge \frac{(logA - x.logB)}{(1-x)}}$$

B = MFR_2 of Fraction (A)
C = MFR_2 of Fraction (B)
A = final MFR_2 (mixture) of multimodal HDPE1
X = weight fraction of Fraction (A)

Flow Rate Ratio (FRR21/2))

[0106]   FRR was determined as the ratio between the MFR_{21} and the MFR_2.

GPC

[0107]   Molecular weight averages (Mz, Mw and Mn), Molecular weight distribution (MWD) and its broadness, described by polydispersity index, PDI= Mw/Mn (wherein Mn is the number average molecular weight and Mw is the weight average molecular weight) were determined by Gel Permeation Chromatography (GPC) according to ISO 16014-1:2003, ISO 16014-2:2003, ISO 16014-4:2003 and ASTM D 6474-12 using the following formulas:

$$M_n = \frac{\sum_{i=1}^{N} A_i}{\sum_{i=1}^{N} (A_i/M_i)} \quad (1)$$

$$M_w = \frac{\sum_{i=1}^{N} (A_i x M_i)}{\sum_{i=1}^{N} A_i} \quad (2)$$

$$M_Z = \frac{\sum_{i=1}^{N}(A_i \times M_i^2)}{\sum_{i=1}^{N}(A_i x M_i)} \quad (3$$

[0108] For a constant elution volume interval ΔV_i, where A_i, and M_i are the chromatographic peak slice area and polyolefin molecular weight (MW), respectively associated with the elution volume, V_i, where N is equal to the number of data points obtained from the chromatogram between the integration limits.

[0109] A high temperature GPC instrument, equipped with either infrared (IR) detector (IR4 or IR5 from PolymerChar (Valencia, Spain), equipped with 3 × Agilent-PLgel Olexis and 1x Agilent-PLgel Olexis Guard columns was used. As the solvent and mobile phase 1,2,4-trichlorobenzene (TCB) stabilized with 250 mg/L 2,6-Di tert butyl-4-methyl-phenol) was used. The chromatographic system was operated at 160 °C and at a constant flow rate of 1 mL/min. 200 μL of sample solution was injected per analysis. Data collection was performed using either Agilent Cirrus software version 3.3 or PolymerChar GPC-IR control software.

[0110] The column set was calibrated using universal calibration (according to ISO 16014-2:2003) with 19 narrow MWD polystyrene (PS) standards in the range of 0,5 kg/mol to 11 500 kg/mol. The PS standards were dissolved at room temperature over several hours. The conversion of the polystyrene peak molecular weight to polyolefin molecular weights is accomplished by using the Mark Houwink equation and the following Mark Houwink constants:

$$K_{PS} = 19 \times 10^{-3} \text{ mL/g}, \quad \alpha_{PS} = 0.655$$

$$K_{PE} = 39 \times 10^{-3} \text{ mL/g}, \quad \alpha_{PE} = 0.725$$

$$K_{PP} = 19 \times 10^{-3} \text{ mL/g}, \quad \alpha_{PP} = 0.725$$

[0111] A third order polynomial fit was used to fit the calibration data.

[0112] All samples were prepared in the concentration range of 0,5 -1 mg/ml and dissolved at 160 °C for 2.5 hours for PP or 3 hours for PE under continuous gentle shaking.

Comonomer contents

Quantification of microstructure by NMR spectroscopy

[0113] Quantitative nuclear-magnetic resonance (NMR) spectroscopy was used to quantify the comonomer content of the polymers.

[0114] Quantitative $^{13}C\{^1H\}$ NMR spectra recorded in the molten-state using a Bruker Advance III 500 NMR spectrometer operating at 500.13 and 125.76 MHz for ^1H and ^{13}C respectively. All spectra were recorded using a ^{13}C optimised 7 mm magic-angle spinning (MAS) probehead at 150°C using nitrogen gas for all pneumatics. Approximately 200 mg of material was packed into a 7 mm outer diameter zirconia MAS rotor and spun at 4 kHz. This setup was chosen primarily for the high sensitivity needed for rapid identification and accurate quantification. {klimke06, parkinson07, castignolles09} Standard single-pulse excitation was employed utilising the NOE at short recycle delays{pollard04, klimke06} and the RS-HEPT decoupling scheme{fillip05,griffin07}. A total of 1024 (1k) transients were acquired per spectra. Quantitative $^{13}C\{^1H\}$ NMR spectra were processed, integrated and relevant quantitative properties determined from the integrals. All chemical shifts are internally referenced to the bulk methylene signal ($\delta+$) at 30.00 ppm.

[0115] The amount of ethylene was quantified using the integral of the methylene ($\delta+$) sites at 30.00 ppm accounting for the number of reporting sites per monomer:

$$E = I_{\delta+} / 2$$

the presence of isolated comonomer units is corrected for based on the number of isolated comonomer units present:

$$Etotal = E + (3*B + 2*H) / 2$$

where B and H are defined for their respective comonomers. Correction for consecutive and non-consecutive commoner

incorporation, when present, is undertaken in a similar way.

[0116] Characteristic signals corresponding to the incorporation of 1-butene were observed and the comonomer fraction calculated as the fraction of 1-butene in the polymer with respect to all monomer in the polymer:

$$fBtotal = (Btotal\ /\ (Etotal + Btotal + Htotal)$$

[0117] The amount isolated 1-butene incorporated in EEBEE sequences was quantified using the integral of the $_*B2$ sites at 38.3 ppm accounting for the number of reporting sites per comonomer:

$$B = I_{*B2}$$

[0118] The amount consecutively incorporated 1-butene in EEBBEE sequences was quantified using the integral of the $\alpha\alpha B2B2$ site at 39.4 ppm accounting for the number of reporting sites per comonomer:

$$BB = 2 * I\alpha\alpha B2B2$$

[0119] The amount non consecutively incorporated 1-butene in EEBEBEE sequences was quantified using the integral of the $\beta\beta B2B2$ site at 24.7 ppm accounting for the number of reporting sites per comonomer:

$$BEB = 2 * I\beta\beta B2B2$$

[0120] Due to the overlap of the $*B2$ and $*\beta B2B2$ sites of isolated (EEBEE) and non-consecutivly incorporated (EEBEBEE) 1-butene respectively the total amount of isolated 1-butene incorporation is corrected based on the amount of non-consecutive 1-butene present:

$$B = I_{*B2} - 2 * I_{\beta\beta B2B2}$$

[0121] The total 1-butene content was calculated based on the sum of isolated, consecutive and non consecutively incorporated 1-butene:

$$Btotal = B + BB + BEB$$

[0122] The total mole fraction of 1-butene in the polymer was then calculated as:

$$fB = (Btotal\ /\ (\ Etotal + Btotal + Htotal)$$

[0123] Characteristic signals corresponding to the incorporation of 1-hexene were observed and the comonomer fraction calculated as the fraction of 1-hexene in the polymer with respect to all monomer in the polymer:

$$fHtotal = (Htotal\ /\ (Etotal + Btotal + Htotal)$$

[0124] The amount isolated 1-hexene incorporated in EEHEE sequences was quantified using the integral of the $_*B4$ sites at 39.9 ppm accounting for the number of reporting sites per comonomer:

$$H = I_{*B4}$$

[0125] The amount consecutively incorporated 1-hexene in EEHHEE sequences was quantified using the integral of the $\alpha\alpha B4B4$ site at 40.5 ppm accounting for the number of reporting sites per comonomer:

$$HH = 2 * I\alpha\alpha B4B4$$

[0126] The amount non consecutively incorporated 1-hexene in EEHEHEE sequences was quantified using the integral of the $\beta\beta B4B4$ site at 24.7 ppm accounting for the number of reporting sites per comonomer:

$$HEH = 2 * I\beta\beta B4B4$$

[0127] The total mole fraction of 1-hexene in the polymer was then calculated as:

$$fH = (Htotal / (Etotal + Btotal + Htotal)$$

[0128] The mole percent comonomer incorporation is calculated from the mole fraction:

$$B [mol\%] = 100 * fB$$

$$H [mol\%] = 100 * fH$$

[0129] The weight percent comonomer incorporation is calculated from the mole fraction:

$$B [wt\%] = 100 * (fB * 56.11) / ((fB * 56.11) + (fH * 84.16) + ((1-(fB + fH)) * 28.05)$$
$$)$$

$$H [wt\%] = 100 * (fH * 84.16) / ((fB * 56.11) + (fH * 84.16) + ((1-(fB + fH)) *$$
$$28.05))$$

References:

[0130]

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Density

[0131] The density was measured according to ISO 1183, and ISO 1872-2 was applied for sample preparation.

Tensile modulus

[0132] Tensile modulus was measured in machine and/or transverse direction according to ISO 527-3 on film samples prepared as described under the Film Sample preparation with film thickness of 20 μm and at a cross head speed of 1 mm/min for the modulus.

Haze

[0133] Haze as a measure for the optical appearance of the films was determined according to ASTM D1003 on film samples with a thickness of 20μm.

DSC Analysis

[0134] Melting temperature Tm and Crystallization temperature Tc were measured with a TA Instrument Q2000 differential scanning calorimetry (DSC) on 5 to 7 mg samples. DSC is run according to ISO 11357 / part 3 /method C2 in a heat / cool / heat cycle with a scan rate of 10 °C/min in the temperature range of -30 to +225°C. Crystallization temperature was determined from the cooling step, while melting temperature (Tm) and melting enthalpy (Hm) are determined from the second heating step.

Examples:

Materials:

[0135] **HDPE (a)**: a bimodal HDPE produced with a ZN catalyst (as disclosed in EP 2994506B1), in a pilot plant, with a configuration of prepolymerisation- loop - gas phase reactor, having MFR$_2$ of 0.8 g/10min, density of 955. 5 kg/m^3. It was pelletized with 500 ppm Irganox 1010 (supplied by BASF), 2000 ppm Irgafos 168 (supplied by BASF), 500 ppm Calcium stearat (CEASIT FI, supplied by Baerlocher) on a twin screw extruder. Production details are presented in Table 1 below.

[0136] **HDPE (b):** a unimodal HDPE with a density of 962 kg/m^3, MFR$_2$ of 12 g/10 min and is (commercially available HDPE from Borealis A/S).

[0137] **HDPE (c):** a bimodal HDPE produced with a ZN catalyst (as disclosed in Example 1 in EP 1378528), in a pilot plant, with a configuration of prepolymerisation- loop - gas phase reactor, having MFR$_2$ of 0.7 g/10min, density of 959.5 kg/m^3. It was pelletized on a twin screw extruder with 1000 ppm of Irganox B561 (a 1:4 mixture of Irganox 1010 and Irgafos 168, produced by BASF) and 1000 ppm Calsium stearate (CEASIT FI, supplied by Baerlocher). Production details are presented in Table 1 below.

[0138] **HDPE (d):** a unimodal HDPE produced in a single gas phase reactor, with a Ziegler-Natta catalyst, details of which are described in EP1780225A1, manufactured by Grace Catalyst AB. The polymerisation conditions are given in Table 2 below. It was pelletized with 1000 ppm of Irganox B225 (supplied by BASF), 700 ppm calciumstearate (CEASIT FI, supplied by Baerlocher) in a twin screw extruder. The blend has a melt flow rate MFR$_2$ of 30 g/10 min, a density of 960 kg/m^3. It has a Mz of 255000 g/mol, a Mw of 52575 g/mol, and a Mw/Mn ratio of 4.96.

[0139] **HDPE (e):** a bimodal HDPE produced with a ZN catalyst (as disclosed in Example 1 in EP 1378528), in a pilot plant, with a configuration of prepolymerisation- loop - gas phase reactor, having MFR$_2$ of 1.5 g/10min, density of 960.7 kg/m^3. It was pelletized with 500 ppm Irganox 1010 (supplied by BASF), 2000 ppm Irgafos 168 (supplied by BASF), 500 ppm Calcium stearat (CEASIT FI, supplied by Baerlocher) on a twin screw extruder. Production details are presented in Table 1 below.

[0140] Table 1 shows the typical polymerisation parameters and final polymer properties for HDPE (a), HDPE (c) and HDPE (e), while Table 2 shows the same for HDPE (d).

Table 1

	HDPE (a)	HDPE (c)	HDPE (e)
Prepoly			
Temp. (°C)	70	70	70
Press. (bar)	57	64	57
H2 (g/h)	5.0	2.0	5.0

(continued)

Loop reactor			
Temp. (°C)	95	95	95
Press. (bar)	55	64	54
C2 conc. (mol%)	3.5	2.8	4.1
H2/C2 (mol/kmol)	430	456	312
Density (kg/m^3)	970	972	971
split %	49.0	45	44
MFR$_2$ (g/10 min)	350	280	214
GPR			
Temp. (°C)	85	85	85
Press. (bar)	20	20	20
H2/C2 (mol/kmol)	110	110	142
C4/C2 (mol/kmol)	25.0	18.8	11
split %	51.0	55	56
Density (kg/m3)	955.5	959.5	960.7
MFR$_2$ (g/10 min)	0.80	0.70	1.5
Pellet			
Density (kg/m3)	955.5	959.5	960.7
MFR$_2$ (g/10 min)	0.8	0.70	1.5
MFR$_{21}$ (g/10 min)	47.4	43.4	81.7
MFR$_{21}$/MFR$_2$	59.2	62	54
MFR in GPR	0.002	0.008	0.5
Density in GPR	941.6	949	952.3

Table 2. Polymerisation details of HDPE (d)

	Unit	HDPE (d)
Reactor pressure	bar	21
Temperature	°C	105
Ethylene partial pres.	bar	7
Butene conc.	C4/C2*100	2.4
Hydrogen conc.	H2/C2*100	50

Composition and Film preparation

[0141]   Six inventive examples and three comparative examples were prepared, with compositions and properties as set out in Table 3. The blending of PEs were done on ZSK 57 and the sheets were done on a Collin 30 lab scale cast film line, with a production rate of 20 kg/h, Chill roll 80°C, melt temperature of 270 °C. In the sheet production step, at the same production rate and melt temperature, blending in the HDPE2 can reduce the melt pressure relative to HDPE1 alone (as shown in Figure 1), meaning higher production rate is possible.

[0142]   Biaxially oriented films were prepared on a Karo 4 lab scale stretch facility. Sheet before stretching was made from a lab scale cast line as described above. The initial sheet thickness was controlled according to the maximum stretch ratio to reach the final film thickness of 20 µm.

[0143] Properties of the films are shown in Table 3. As can be seen, the IEs give excellent stiffness and optical balance, as reflected by the Tensile Modulus and Haze results, when both properties were determined on 20 μm thick samples. Another advantage of the present invention is that higher stretch ratio is possible when the polymer blends according to the present invention are used.

Table 3

	CE1	IE1	IE2	IE3	IE4	IE5	IE6	CE2	CE3
HDPE (a) (wt%)	100	80	85	80					
HDPE (b) (wt%)		20							
HDPE (c) (wt%)					85	80	75	100	
HDPE (d) (wt%)			15	20	15	20	25		
HDPE (e) (wt%)									100
MFR_2 (g/10 min)	0.8	1.4	1.1	1.3	1.1	1.2	1.4	0.7	1.5
MFR_{21} (g/10 min)	47.4		71.5	83.8	55.4	67.19	79.2	43.4	81.7
MFR_{21}/MFR_2	59.2		65	67	52	57	57	62	54
Tc (°C)	117		117	117	118	118	118	118	118
Tm(°C)	131		131	131	134	132	132	133	133
Hm (J/g)	210		205	207	213	220	220	212	215
Density (kg/m^3)	955.5	958	955.8	956.2	960	959.9	960.1	959.5	960.7
Mw	127000		120500	112500	119500	116500	111500	133000	113000
Mz	708000		703000	635500	621500	646000	611500	697000	566000
MWD	16.09		15.16	14.09	11.99	11.53	10.88	13.34	10.02
Mz/Mw	5.57		5.83	5.65	5.20	5.55	5.48	5.24	5.01
Sheet									
Throughput (kg/h)	20		20	20	20	20	20	20	20
T(°C)	271		271	272	271	270	270	271	270
P (Bar)	175		156	143	171	159	149	192	152
BOPE									
Max ratio	8.5x8.5	6.5 × 6.5	8.5x8.5	8.5x8.5	10×10	10×10	10×10	10×10	7.5x7.5
T(°C)	125		125	125	129.5	129.5	129.5	129.5	129.5
TM/MD (MPa)	1694	2215	2062	1763	2183	1781	1761	1888	1561
TM/TD (MPa)	1669		1762	1652	1771	1708	1633	1766	1536
Haze (%)	4	3.4	4	4	14	13	12	15	21

Claims

1. A biaxially oriented film comprising a multimodal high density polyethylene (HDPE1), wherein HDPE1 has a density determined according to ISO 1183 in the range of 952 to 968 kg/m^3 and an MFR_2 determined at 190 °C according to ISO 1133 of 0.3 to 3.0 g/10 min, and wherein HDPE1 comprises at least two fractions:

    (A) 30 to 70 wt%, relative to the total weight of HDPE1, of a lower molecular weight fraction being a polyethylene with a density in the range of 955 to 980 kg/m^3 and an MFR_2 of 100 to 2000 g/10 min; and
    (B) 30 to 70 wt%, relative to the total weight of HDPE1, of a higher molecular weight fraction being a polyethylene with a density in the range of 925 to 970 kg/m^3 and an MFR_2 of 0.0001 to 1.0 g/10 min;

and wherein said film further comprises 1 to 30 wt%, relative to the total weight of the film, of a second HDPE (HDPE2) with a density in the range of 955 to 985 kg/m^3 and an MFR_2 of 5 to 100 g/10 min, and which is different to HDPE1.

2. The biaxially oriented article as claimed in claim 1 wherein said film is a monolayer film.

3. The biaxially oriented film as claimed in claim 1 or 2, wherein

   a) fraction (A) is present in an amount of 35 to 50 wt%, preferably 40 to 50 wt%, relative to the total weight of HDPE1, and/or
   b) fraction (B) is present in an amount of be 50 to 65 wt%, preferably 50 to 60 wt%, relative to the total weight of HDPE1.

4. The biaxially oriented film as claimed in any of claims 1 to 3, wherein HDPE1 has an MFR_2 determined at 190 °C according to ISO 1133 of 0.4 to 2.5 g/10min, preferably from 0.5 to 2.0 g/10min, and more preferably from 0.6 to 1.0 g/10 min.

5. The biaxially oriented film as claimed in any of claims 1 to 4, wherein HDPE1 is bimodal and consists of fractions (A) and (B).

6. The biaxially oriented film as claimed in any of claims 1 to 5, wherein the lower molecular weight fraction (A) is an ethylene homopolymer.

7. The biaxially oriented film as claimed in any of claims 1 to 6, wherein the higher molecular weight fraction (B) is an ethylene copolymer with at least one alpha-olefin comonomer, preferably 1-butene.

8. The biaxially oriented film as claimed in any of claims 1 to 7, wherein said HDPE1 is present in an amount of 70 to 99 wt%, preferably 75 to 95 wt% relative to the total weight of the film.

9. The biaxially oriented film as claimed in any of claims 1 to 8, wherein said HDPE2 is present in an amount of 1 to 30 wt%, preferably 5 to 25 wt%, relative to the total weight of the film.

10. The biaxially oriented film as claimed in any of claims 1 to 9, wherein said HDPE2 has a density of 957 to 980 kg/m^3, preferably 960 to 970 kg/m^3.

11. The biaxially oriented film as claimed in any of claim 1 to 10, wherein said HDPE2 has an MFR_2 of 8 to 60 g/10 min, preferably 10 to 50 g/10 min.

12. The biaxially oriented film as claimed in any of claims 1 to 11, wherein said HDPE2 is an ethylene copolymer, preferably a copolymer of ethylene and at least one C_{3-12} alpha-olefin comonomer(s).

13. The biaxially oriented film as claimed in any of claims 1 to 12, wherein said film has a tensile modulus (TM), determined according to ISO 527-3 on 20 μm films in the machine direction (MD) of at least 1000 MPa to 4000 MPa.

14. The biaxially oriented film as claimed in any of claims 1 to 13, wherein said film has a stretch ratio in the machine direction (MD) and/or transverse direction (TD) of at least 7.0 times.

15. A laminated film structure comprising a biaxially oriented film as defined in any of claims 1 to 14 laminated to a substrate.
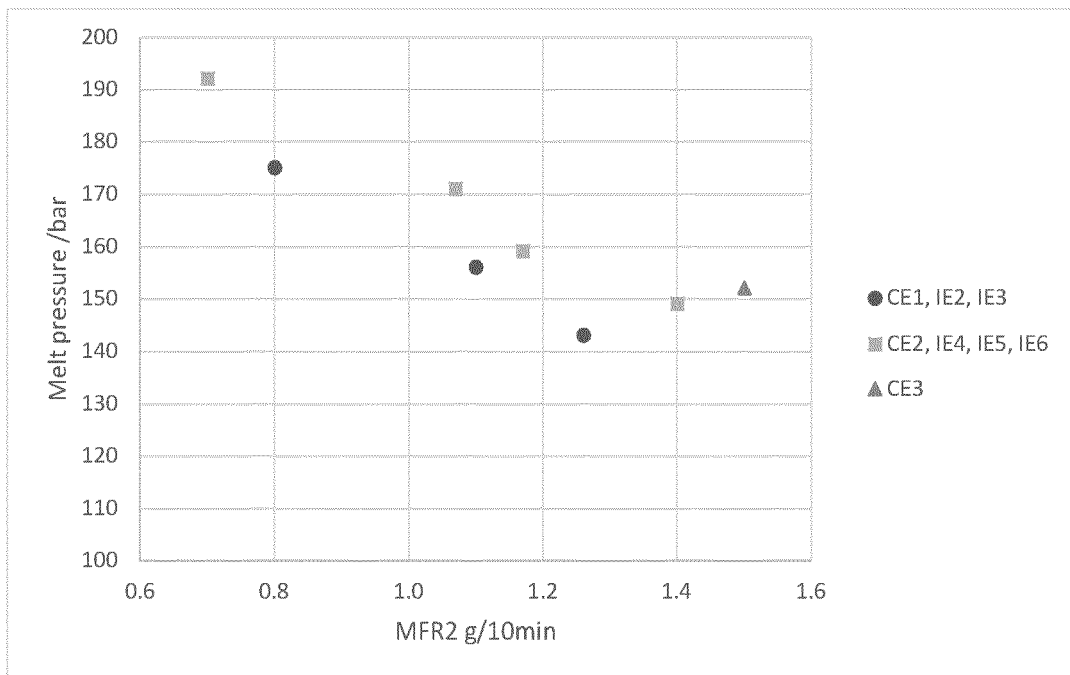
FIG 1

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			C08L C08J

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	6 February 2023	Pamies Olle, Silvia

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